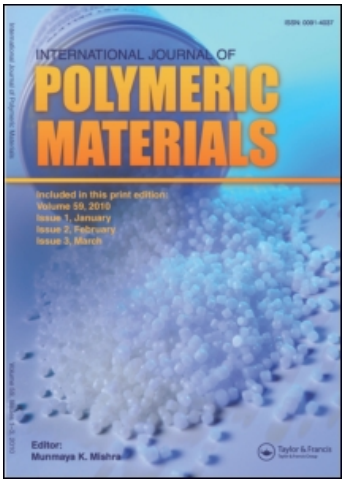

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SYNTHESIS AND APPLICATIONS OF NOVEL FLUOROALKYL END-CAPPED OLIGOMERS CONTAINING 3,5-DIMETHYL-4-HYDROXYBENZYL AND 3-(2*H*-BENZOTRIAZOL-2-yl)-4-HYDROXYPHENYL SEGMENTS

Hideo Sawada[a]; Nobuhito Kawasaki[b]; Kazuo Sasazawa[c]; Tokuzo Kawase[d]
[a] Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki, Japan [b] Department of Chemistry, Faculty of Advanced Engineering, Nara National College of Technology, Yamatokoriyama, Nara, Japan [c] Central R & D Laboratories, Taiyo Yuden Co., Ltd., Sakae-Cho, Takasaki, Gunma, Japan [d] Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan

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SYNTHESIS AND APPLICATIONS OF NOVEL FLUOROALKYL END-CAPPED OLIGOMERS CONTAINING 3,5-DIMETHYL-4-HYDROXYBENZYL AND 3-(2*H*-BENZOTRIAZOL-2-YL)-4-HYDROXYPHENYL SEGMENTS

Hideo Sawada
Department of Materials Science and Technology,
Faculty of Science and Technology, Hirosaki University,
Hirosaki, Japan

Nobuhito Kawasaki
Department of Chemistry, Faculty of Advanced Engineering,
Nara National College of Technology,
Yamatokoriyama, Nara, Japan

Kazuo Sasazawa
Central R & D Laboratories,
Taiyo Yuden Co., Ltd.,
Sakae–Cho, Takasaki, Gunma, Japan

Tokuzo Kawase
Department of Chemistry and Materials Technology,
Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto, Japan

New fluoroalkyl end-capped co-oligomers containing 3,5-dimethyl-4-hydroxybenzyl segments [R_F–(DMHB)$_x$–(DMAA)$_y$-R_F] were prepared by the reactions of fluoroalkanoyl peroxides with N-*(3,5-dimethyl-4-hydroxybenzyl)methacrylamide [DMHB] and* N,N-*dimethylacrylamide (DMAA). Similarly, fluoroalkyl end-capped homo- and co-oligomers containing 3-(2*H-*benzotriazol-2-yl)-4-hydroxyphenyl segments [R_F-(BTRI)$_x$-(Co-M)$_y$-R_F] were prepared by the reactions of fluoroalkanoyl peroxides with 2-[3-(2*H*–*benzotriazol-2-yl)-4-hydroxyphenyl]ethyl*

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Address correspondence to Hideo Sawada, Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan. E-mail: hideosaw@cc.hirosaki-u.ac.jp

methacrylate [BTRI] and co-monomers [Co-M] such as acrylic acid (ACA), DMAA, and acryloylmorpholine (ACMO). The fluoroalkyl end-capped DMHB and BTRI co-oligomers thus obtained were soluble not only in water but also in common organic solvents. In addition, these fluorinated co-oligomers were able to reduce the surface tension of 0.1 N NaOH solutions quite effectively to around 20 mN/m levels, although the corresponding non-fluorinated co-oligomers were not effective in reducing the surface tension of 0.1 N NaOH solutions. A modified polystyrene film surface treated with these fluoroalkyl end-capped DMHB and BTRI co-oligomers was found to exhibit a good oleophobicity imparted by fluorine with an excellent hydrophilicity. XPS analyses showed that end-capped fluoroalkyl groups in R_F-$(BTRI)_n$-R_F homo-oligomer were arranged regularly above the modified polystyrene surface. Of particular interest, it was demonstrated that the self-assembled molecular aggregates formed by R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomers could interact strongly with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as a guest molecule to form a host–guest intermolecular complex, though such a host–guest interaction was not observed in the corresponding non-fluorinated DMHB co-oligomer.

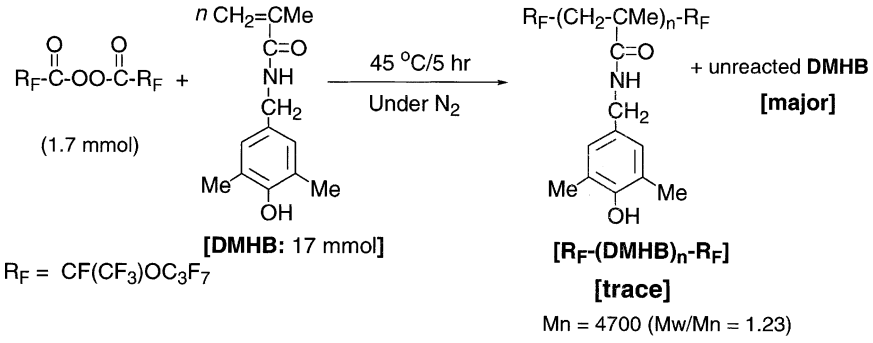
Keywords: fluorinated oligomer, oligomeric surfactant, 3,5-Dimethy-4-hydroxybenzyl segment, 3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl segments, surface tension, surface modification, oleophobicity, hydrophilicity, XPS, host–guest interaction

INTRODUCTION

Long fluoroalkylated surfactants bearing aromatic nuclei are known to possess a good surface active property [1]. These fluorinated surfactants exhibit a good solubility in water; however, the development of oil-soluble fluorinated surfactants bearing aromatic nuclei have been hitherto limited [1]. Therefore, it is of particular interest to explore novel amphiphilic fluoroalkylated surfactants containing aromatic nuclei. In addition, there has been a considerable interest in polymeric surfactants that exhibit a variety of unique properties such as high dispersing, aggregates, and emulsion properties that cannot be achieved by low-molecular-weight surfactants [2]. In view of the development of novel fluorinated surfactants, the synthesis of fluoroalkylated polymeric surfactants bearing aromatic nuclei is expected to have high potential for new fluorinated functional materials. This article reports on the synthesis and applications of novel fluoroalkyl end-capped amphiphilic oligomers containing aromatic segments such as 3,5-dimethyl-4-hydroxybenzyl and 3-2*H*-benzotriazol-2-yl)-4-hydroxyphenyl groups.

RESULTS AND DISCUSSION

Phenol derivatives are interesting materials, exhibiting some important characteristics such as the antioxidative property. Thus, the



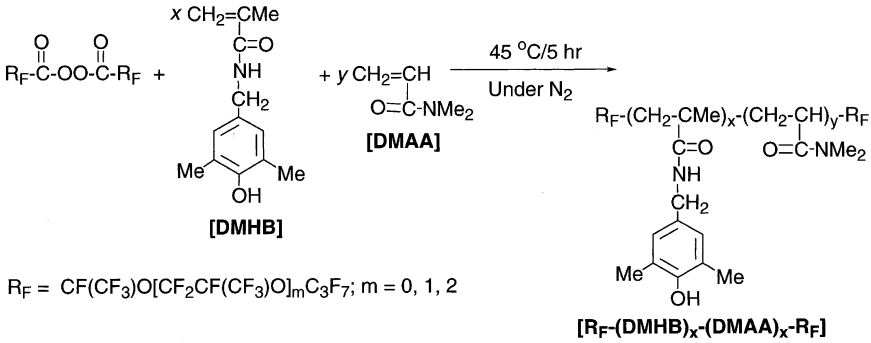
SCHEME 1

synthesis of fluoroalkylated polymeric surfactants containing phenol segments is interesting. First, the authors tried to react fluoroalkanoyl peroxide with methacrylamide monomer possessing phenol segments [*N*-(3,5-dimethyl-4-hydroxybenzyl)methacrylamide: DMHB]. The reaction of fluoroalkanoyl peroxide with DMHB was carried out at 45°C for 5 h under nitrogen. See Scheme 1 for the reaction and results.

As shown in Scheme 1, fluoroalkanoyl peroxide reacted with DMHB to produce fluoroalkyl end-capped DMHB oligomer; however, the yield of the expected product was extremely low, and the starting materials of DMHB was quantitatively recovered. Previously, the authors reported that fluoroalkanoyl peroxide can suffer a single electron transfer reaction from aromatic compounds to the peroxide to cause a aromatic fluoroalkylation [3]. From these findings, it is strongly suggested that fluoroalkanoyl peroxide could react with DMHB in the presence of a well-known aliphatic radical polymerizable co-monomer such as *N*,*N*-dimethylacrylamide (DMAA) to afford fluoroalkyl end-capped DMHB co-oligomer. In fact, as shown in Scheme 2 and Table 1, the reactions of fluoroalkanoyl peroxides with DMHB and DMAA were found to proceed under very mild conditions to give fluoroalkyl end-capped DMHB-DMAA co-oligomers in 8 to 69% isolated yields.

Phenol derivative containing benzotriazole segment is also as attractive as DMHB, because this compound is known to have ultraviolet radiation absorption. The authors tried to react methacrylate monomer containing benzotriazole segment [2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate: BTRI] with fluoroalkanoyl peroxides, and the results are shown in Schemes 3 and 4 and Table 2.

As shown in Scheme 3, homooligomerization of BTRI with fluoroalkanoyl peroxide was found to proceed under very mild conditions to give fluoroalkyl end-capped BTRI homooligomer in 39% isolated



SCHEME 2

yield. Additionally, co-oligomerizations of BTRI with fluoroalkanoyl peroxides by the use of co-monomers such as acrylic acid (ACA), DMAA, and acryloylmorpholine (ACMO) afforded fluoroalkyl end-capped BTRI co-oligomers in 16 to 98% isolated yields under similar conditions (see Scheme 4 and Table 2). In the oligomerization of BTRI, could be observed the radical homooligomerization of BTRI with fluoroalkanoyl peroxide, although the homooligomerization of DMHB with this peroxide was not observed. This reflects the fact that the radical reactivity of BTRI monomer toward fluoroalkanoyl peroxide is superior to that of DMHB.

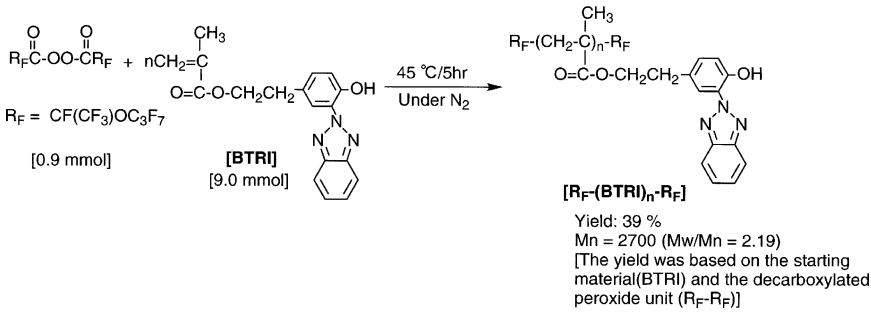
The authors have tested a variety of fluoroalkyl end-capped DMHB and BTRI oligomers, listed in Tables 1 and 2 and Scheme 3, for their solubility. Fluoroalkyl end-capped DMHB-DMAA co-oligomers exhibited a good solubility in not only water but also in common organic solvents such as methanol, ethanol, tetrahydrofuran, dimethyl sulfoxide, chloroform, benzene, toluene, and ethyl acetate. Fluoroalkyl end-capped BTRI homooligomer [R_F-$(BTRI)_n$-R_F] was not soluble in water, but this oligomer was easily soluble in tetrahydrofuran, chloroform. benzene, toluene, dimethyl sulfoxide, and ethyl acetate. On the other hand, R_F-$(BTRI)_x$-$(DMAA)_y$-R_F co-oligomers were soluble in water and common organic solvents such as methanol, ethanol, tetrahydrofuran, chloroform, benzene, toluene, dimethyl sulfoxide, and ethyl acetate. The solubility of R_F-$(BTRI)_x$-$(ACMO)_y$-R_F co-oligomers was inferior to that of R_F-$(BTRI)_x$-$(DMAA)_y$-R_F, and these co-oligomers were not soluble in water. However, these co-oligomers were easily soluble in organic solvents such as tetrahydrofuran, chloroform, benzene, toluene, dimethyl sulfoxide, and ethyl acetate.

The good solubility of the present fluoroalkyl end-capped DMHB and BTRI co-oligomers is applicable to novel fluorinated polymeric

TABLE 1 Reactions of Fluoroalkanoyl Peroxides with DMHB and DMAA

No.	R_F in Peroxide (mmol)	DMHB (mmol)	DMAA (mmol)	[Yield (%)][a]	Product Mn(Mw/Mn)	Product [x:y][b]
1	$CF(CF_3)OC_3F_7$ 2.8	2.3	28	68	1370 (2.25)	[4:96]
2	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ 2.8	2.3	28	19	1560 (1.09)	[4:96]
3	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ 2.8	2.3	28	8	2220 (1.17)	[2:98]

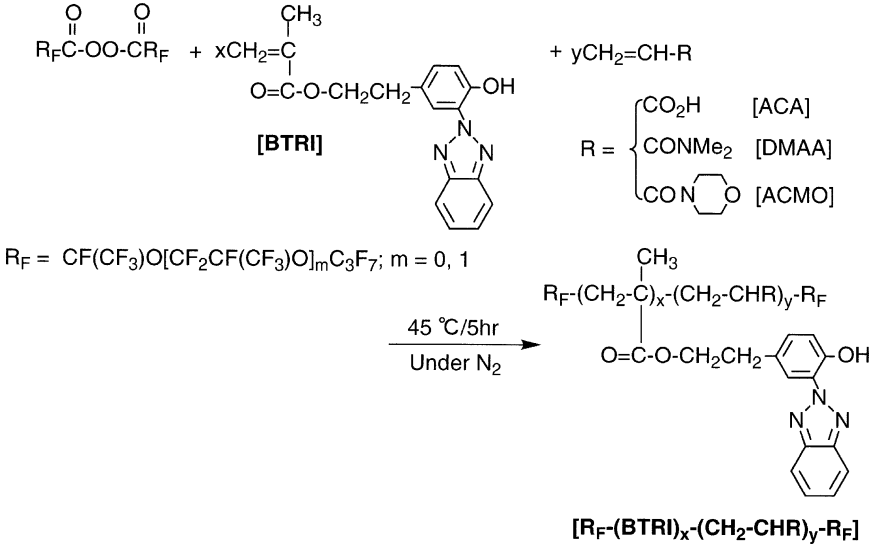
[a]The yields were based on the starting materials: DMHB, DMAA, and the decarboxylated peroxide unit (R_F-R_F).
[b]Co-oligomerization ratio was determined by ^{1}H-NMR.



SCHEME 3

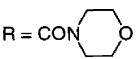
surfactant containing aromatic nuclei. In fact, the authors have measured the surface tension of 0.1 N NaOH solutions of R_F-(DMHB)$_x$-(DMAA)$_y$-R_F and R_F-(BTRI)$_x$-(ACA)$_y$-R_F with Wilhelmy plate method at 30°C, and the results are shown in Figures 1 and 2.

As shown in Figure 1, R_F-(DMHB)$_x$-(DMAA)$_y$-R_F co-oligomers were able to reduce the surface tension of 0.1 N NaOH solution quite effectively to around 20 mN/m levels with a clear break point resembling CMC (critical micelle concentration), although the corresponding non-fluorinated -(DMHB)$_x$-(DMAA)$_y$- co-oligomer was not effective in



SCHEME 4

TABLE 2 Reactions of Fluoroalkanoyl Peroxides with BTRI and Co-Monomers (CH_2=CHR)

No.	R_F in Peroxide (mmol)	BTRI (mmol)	CH_2=CHR (mmol)	[Yield (%)][a]	Product Mn(Mw/Mn)	Product [x:y][b]
4	$CF(CF_3)OC_3F_7$		R = CO_2H			
	1.6	1.6	16	22	6800 (1.27)	[3:97]
5	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
	1.6	1.6	16	16	7800 (1.22)	[2:98]
6	$CF(CF_3)OC_3F_7$		R = $CONMe_2$			
	1.6	1.6	16	94	5700 (1.30)	[11:89]
7	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
	1.6	1.6	16	97	4000(1.23)	[7:93]
8	$CF(CF_3)OC_3F_7$					
	1.6	1.6	16	98	7300 (1.30)	[8:92]
9	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
	1.6	1.6	16	94	8200 (1.29)	[7:93]

[a]The yields were based on the starting materials: BTRI, co-monomer, and the decarboxylated peroxide unit (R_F-R_F).
[b]Co-oligomerization ratio was determined by ^{1}H-NMR.

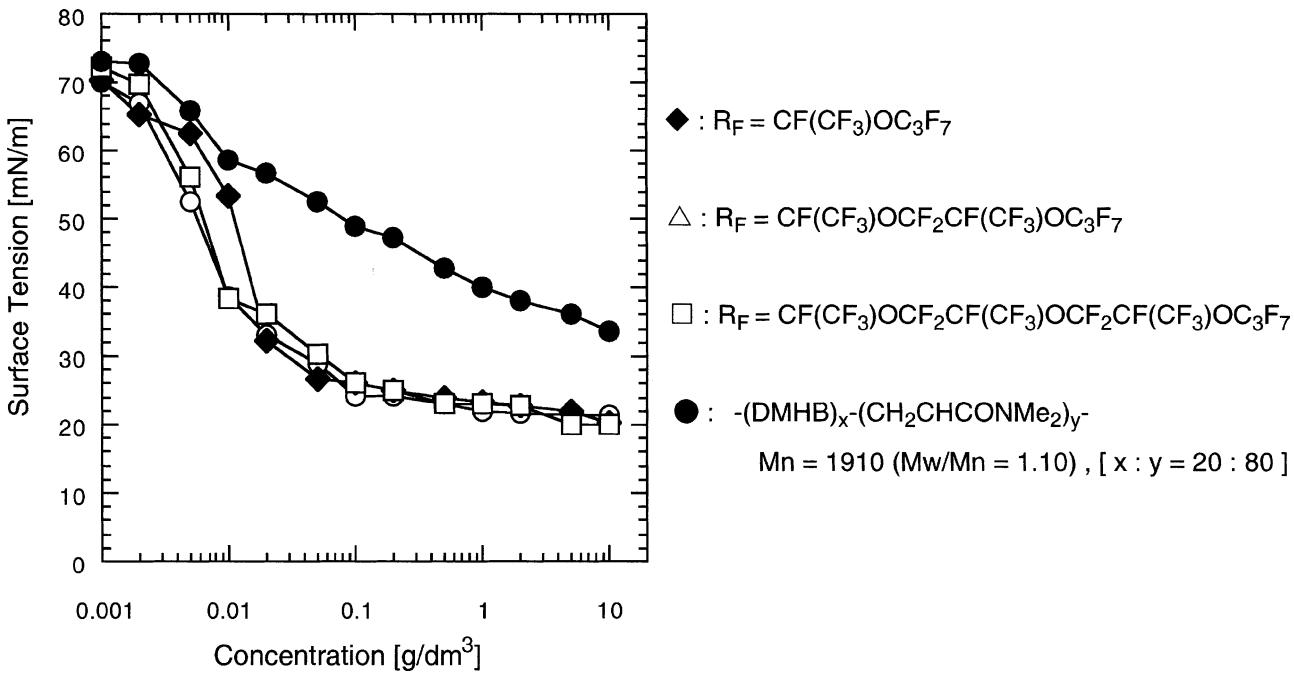


FIGURE 1 Surface tension of 0.1 N NaOH solutions of R_F-(DMHB)$_x$-($CH_2CHCONMe_2$)$_y$-R_F at 30°C.

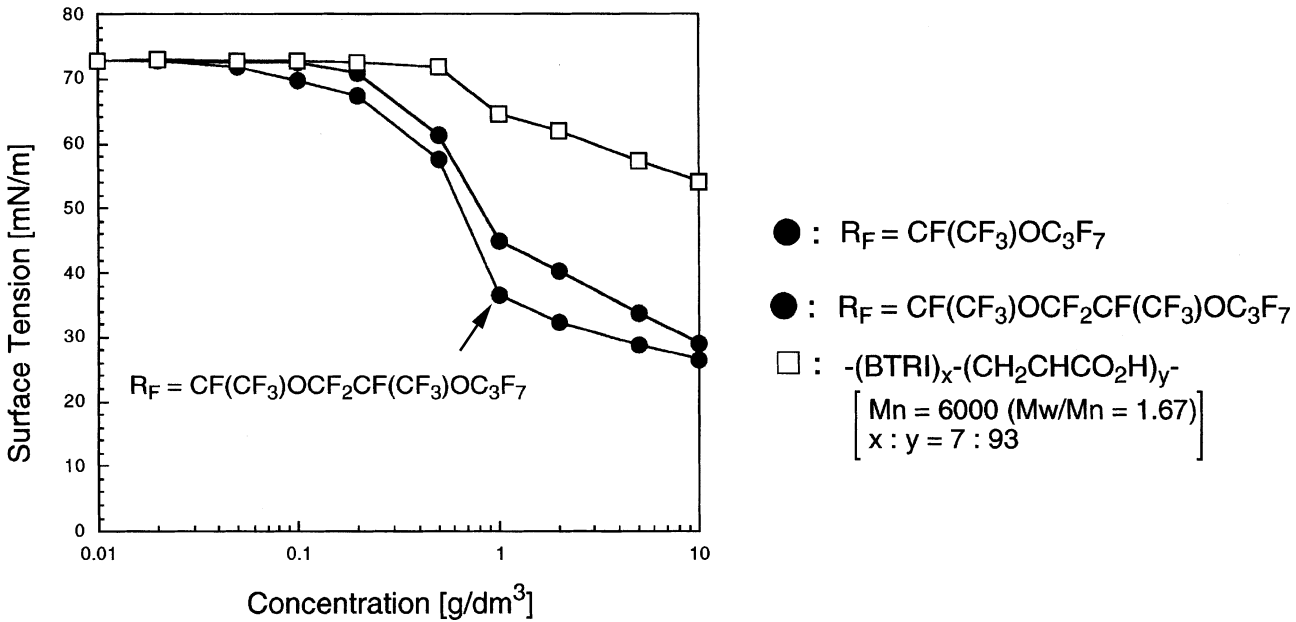


FIGURE 2 Surfce tension of 0.1 N NaOH solutions of R_F-(BTRI)$_x$-(CH_2CHCO_2H)$_y$-R_F at 30°C.

reducing the surface tension of 0.1 N NaOH. A similar result was obtained in measuring the surface tension of 0.1 N NaOH solution of R_F-$(BTRI)_x$-$(ACA)_y$-R_F co-oligomers at 30°C, and fluorinated BTRI co-oligomers were found to have a good surfactant property in comparison with that of the corresponding non-fluorinated co-oligomer: -$(BTR)_x$-$(ACA)_y$- (see Figure 2).

As mentioned earlier, the present fluorinated co-oligomers have not only a good surfactant property but also a good solubility in common organic solvents. Thus, these fluorinated co-oligomers are expected to develop into new fluorinated surface active compounds for common polymeric materials such as polystyrene (Pst). Fluoroalkyl end-capped DMHB and BTRI co-oligomers were tested for surface activity as a new type of surface modification agents.

Contact angles for dodecane on the cast films of Pst treated with R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomers (see Table 3), and fluoroalkyl end-capped BTRI homo- (see Table 4) and co-oligomers (see Table 5) showed a significantly large value (18 to 68°) compared with that (0°) of the corresponding non-fluorinated co- and homooligomers or that of the non-treated Pst (0°). These values were found to increase with increasing the length of end-capped fluoroalkyl groups in co-oligomers (see Tables 3 and 5). In each oligomer, time dependence of contact angle of dodecane was not observed. These results suggest that fluoroalkyl end-capped DMHB and BTRI oligomers should exhibit a markedly strong oleophobicity on the Pst surface, though these co-oligomers possess highly oleophilic aromatic moieties.

Of particular interest, a strong time dependence of contact angle of water was observed in fluoroalkyl end-capped DMHB and BTRI co-oligomers as in Tables 3 and 5. The contact angles of water were found to decrease sharply from 33 to 10° to 19 to 0°. In contrast, the corresponding non-fluorinated co-oligomers and R_F-$(BTRI)_n$-R_F homo-oligomer were not able to decrease the contact angle of water effectively. Thus, these fluorinated co-oligomers were demonstrated to possess markedly strong hydrophilicity on their surface, though these co-oligomers have a strong oleophobic fluroroalkyl group. These results suggest that at the interface with water, hydrophobic fluoroalkyl segments are easily replaced by the strongly hydrophilic segments such as carboxy, dimethylaminocarbonyl [$Me_2NC(=O)$-], and morpholino groups. The hydrophilic segments in co-oligomers should be arranged regularly on the Pst surface. It takes about 30 min to replace the fluoroalkyl groups by the hydrophilic segments when the environment is changed from air to water.

In order to determine the surface arrangement of fluoroalkyl groups in co-oligomers on the Pst surface, the authors have analyzed the Pst

TABLE 3 Contact Angles of Dodecane and Water on Polystyrene Films Treated with $R_F-(DMHB)_x-(DMAA)_y-R_F$[a]

	Contact Angle (Degree)							
R_F in Oligomer	Dodecane	0 min	5 min	10 min	Water 15 min	20 min	25 min	30 min
R_F-$(DMHB)_x$-$(DMAA)_y$-R_F								
$CF(CF_3)OC_3F_7$	42	33	32	29	25	22	20	18
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	56	13	7	6	5	5	0	0
$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	68	10	10	8	8	4	0	0
$-(DMHB)_x-(DMAA)_y-$[b]	0	68	64	61	61	61	61	61

[a]Concentration of co-oligomer based on polystyrene is 1% (m/m).
[b]MN = 1910 (Mw/Mn = 1.10); x:y = 20:80.

TABLE 4 Contact Angles of Dodecane and Water on Polystyrene Films Treated with R_F-$(BTRI)_n$-R_F[a]

	Contact angle (degree)							
R_F in Oligomer	Dodecane	0 min	5 min	10 min	Water 15 min	20 min	25 min	30 min
$CF(CF_3)OC_3F_7$ -$(BTRI)_n$	18	80	78	75	70	67	65	63
Mn = 13800 (Mw/Mn = 1.53)	0	77	71	71	71	71	71	71
Non-treated polystyrene	0	88	86	86	86	86	86	86

[a]Concentration of oligomer based on Polystyrene is 1% (m/m).

TABLE 5 Contact Angles of Dodecane and Water on Polystyrene Films Treated with R_F-$(BTRI)_x$-$(Co\text{-}M)_y$-R_F[a]

	Contact angle (degree)							
R_F in Oligomer	Dodecane	0 min	5 min	10 min	Water 15 min	20 min	25 min	30 min
R_F-$(BTRI)_x$-$(ACA)_y$-R_F								
$CF(CF_3)OC_3F_7$	49	33	30	27	25	25	21	18
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	65	18	10	8	5	3	0	0
-$(BTRI)_x$-$(ACA)_y$-[b]	0	82	82	81	80	80	80	80
R_F-$(BTRI)_x$-$(DMAA)_y$-R_F								
$CF(CF_3)OC_3F_7$	35	25	19	17	13	13	10	10
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	55	16	12	7	6	5	4	3
-$(BTRI)_x$-$(DMAA)_y$-[c]	0	73	73	73	73	70	70	70
R_F-$(BTRI)_x$-$(ACMO)_y$-R_F								
$CF(CF_3)OC_3F_7$	42	32	32	27	26	21	21	19
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	50	27	15	15	10	9	5	5
-$(BTRI)_x$-$(ACMO)_y$-[d]	0	73	73	73	73	66	66	66

[a]Concentration of co-oligomer based on polystyrene is 1% (m/m).
[b]Mn = 8000 (Mw/Mn = 1.67); x:y = 7:93.
[c]Mn = 2200 (Mw/Mn = 2.09); x:y = 10:90.
[d]Mn = 27200 (Mw/Mn = 1.38); x:y = 6:94.

film modified by R_F-$(BTRI)_n$-R_F homooligomer (film thickness: 200 μm) by the use of the XPS (*X*-ray photoelectron spectroscopy) technique, and the amounts of fluorine (F_{ls}), nitrogen (N_{ls}), and oxygen (O_{ls}) at the surface were also estimated. These results are shown in Figure 3.

As shown in Figure 3, interestingly, the relative peak area of fluorine was found to decrease rapidly with increase of the etching time, and the peak of F_{ls} completely disappeared after 5 min of etching (etching rate is about 50 Å/min). A similar tendency was observed in the peaks of N_{ls} and O_{ls} in R_F-$(BTRI)_n$-R_F homooligomer, and the relative peak area of each peak decreased with increase of the etching time. On the other hand, the relative peak area of N_{ls} in the corresponding non-fluorinated BTRI homooligomer: -$(BTRI)_n$- did not change very much with the increase of the etching time. These results strongly suggest that fluoroalkyl groups in R_F-$(BTRI)_n$-R_F homooligomers should be preferentially arranged above the Pst surface, and in contrast, the corresponding BTRI homooligomer is homogeneously dispersed in the modified Pst film.

The authors have recently reported that fluoroalkyl end-capped oligomers can form self-assembled molecular aggregates with the aggregations of the end-capped fluoroalkyl groups in aqueous and organic media [4]. In particular, they have found that fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers can form self-assembled molecular aggregates with the aggregations of end-capped fluoroalkyl segments to recognize hydrophilic amino and dimethylamino compounds such as methylene blue, methyl orange, and acriflavine hydrochloride as guest molecule [5]. Hitherto, it is well known that tetracyanoethylene (TCNE) can interact with aromatic compounds such as anisole, hexamethylbenzene, and chloranil to form charge-tranfer complexes [6]. Thus, it is expected that the self-assembled molecular aggregates formed by fluoroalkyl end-capped DMHB co-oligomers should interact with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as a guest molecule. From this point of view, the authors have studied the potential of fluoroalkyl end-capped co-oligomers as a host system for a guest molecule (TCNQ). They have measured UV-vis spectra of tetrahydrofuran solutions to TCNQ in the presence of R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomers, and the results are shown in Figure 4.

As shown in Figure 4, the decrease of absorbance ($\lambda_{max} = 400$ nm) of TCNQ by the addition of R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomer, can be observed and new red-shifted peaks appeared around $\lambda_{max} = 500$ nm. The absorbance of the new peaks increased with increasing interaction time of TCNQ with the co-oligomer. Similar results were obtained in R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomers:

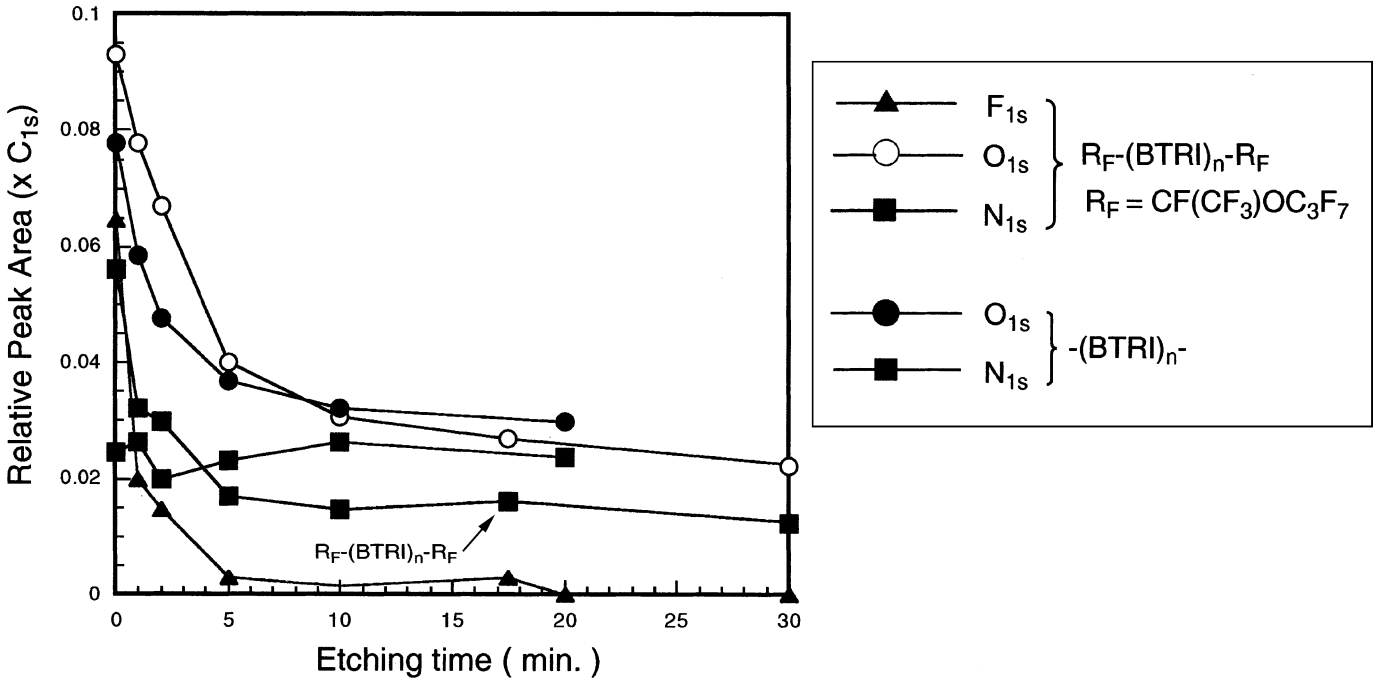
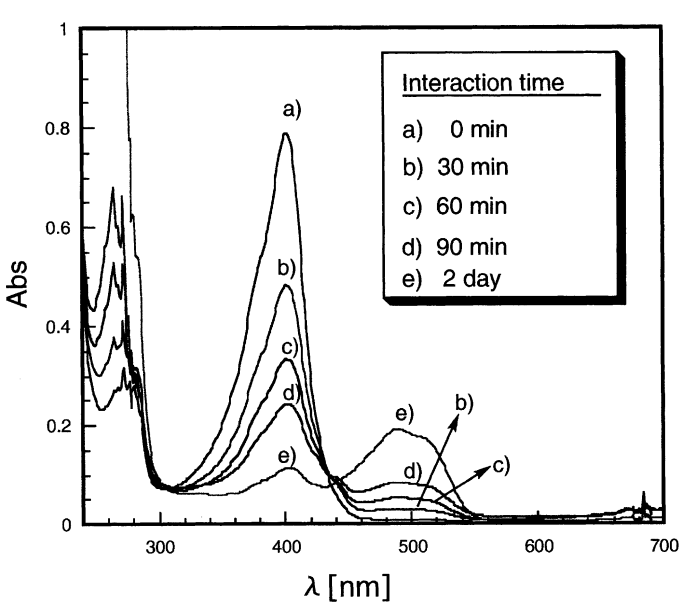
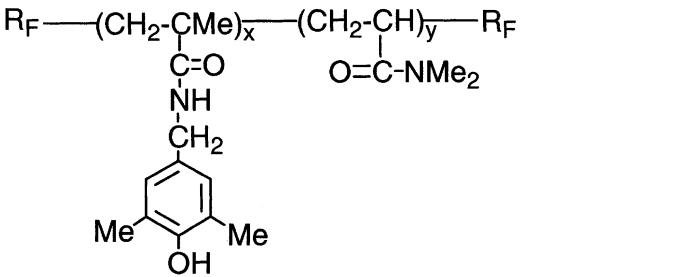


FIGURE 3 Depth profiles of R_F-(BTRI)$_x$-R_F and -(BTRI)$_x$- measured by XPS.

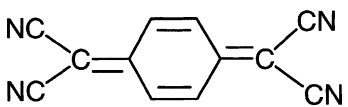




[R_F-(DMHB)$_x$-(DMAA)$_y$-R_F]

$R_F = CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

9.01×10^{-5} mol/dm^3



[TCNQ]

1.67×10^{-5} mol/dm

FIGURE 4 UV spectra of THF solutions of TCNQ in the presence of R_F-(DMHB)$_x$-(DMAA)$_y$-R_F co-oligomers.

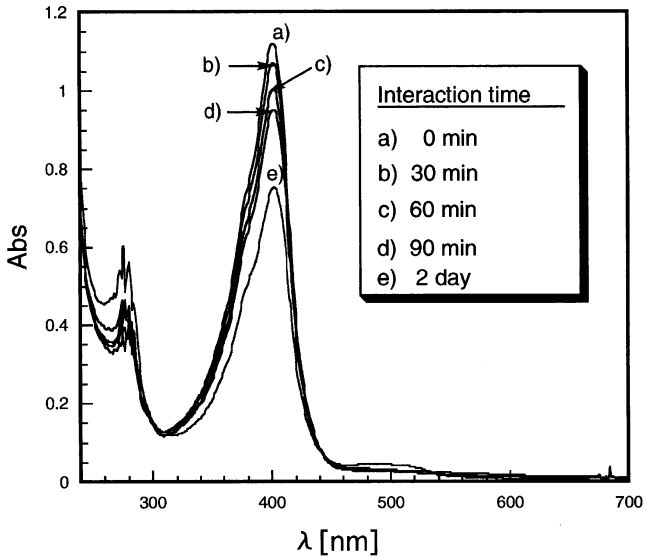
$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ and $CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (data not shown). On the other hand, the corresponding non-fluorinated -$(DMHB)_x$-$(DMAA)_y$- co-oligomer was not able to interact with TCNQ to afford new red-shifted peak around 500 nm under similar conditions (see Figure 5). These findings suggest that molecular assemblies formed by R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomer could interact strongly with TCNQ as a guest molecule to form host–guest intermolecular complexes as illustrated in Figure 6. On the other hand, non-fluorinated -$(DMHB)_x$-$(DMAA)_y$-would not form such self-assemblies to interact effectively with TCNQ.

In conclusion, the authors have succeeded in creating a variety of fluoroalkyl end-capped oligomers containing aromatic nuclei such as 3,5-dimethyl-4-hydroxybenzyl [DMHB] and 3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl [BTRI] groups by the use of fluoroalkanoyl peroxide as a key intermediate. The fluoroalkyl end-capped DMHB and BTRI cooligomers thus obtained were in general soluble in water and common organic solvents. Therefore, these fluorinated co-oligomers are applicable as novel polymeric surfactants containing aromatic nuclei. In fact, these fluorinated co-oligomers were able to reduce the surface tension of 0.1 N NaOH quite effectively, though the corresponding non-fluorinated co-oligomers were not effective for reducing the surface tension of 0.1 N NaOH. Fluoroalkyl end-capped DMHB and BTRI co-oligomers were also applied as surface modifiers for common polymeric materials such as poylstyrene, and the modified polystyrene surface with these fluorinated co-oligomers were shown to exhibit not only a good oleophobicity imparted by fluorine but also a strong hydrophilicity. Especially, XPS analysis showed that end-capped fluoroalkyl segments in R_F-$(BTRI)_n$-R_F homooligomer could be arranged preferentially on the polystyrene surface, although the corresponding non-fluorinated BTRI homooligomer was homogeneously dispersed in the modified polystyrene. Of particular interest, the self-assembled molecular aggregates formed by R_F-$(DMHB)_x$-$(DMAA)_y$-R_F co-oligomers could interact with TCNQ as a guest molecule to form host–guest intermolecular complexes. In contrast, the corresponding non-fluorinated co-oligomer was not able to interact with TCNQ under similar conditions.

EXPERIMENTAL

Measurements

Fourier-transform infrared (FTIR) spectra were measured using a HORIBA FT-300 FT-IR spectrophotometer. NMR spectra and molecular



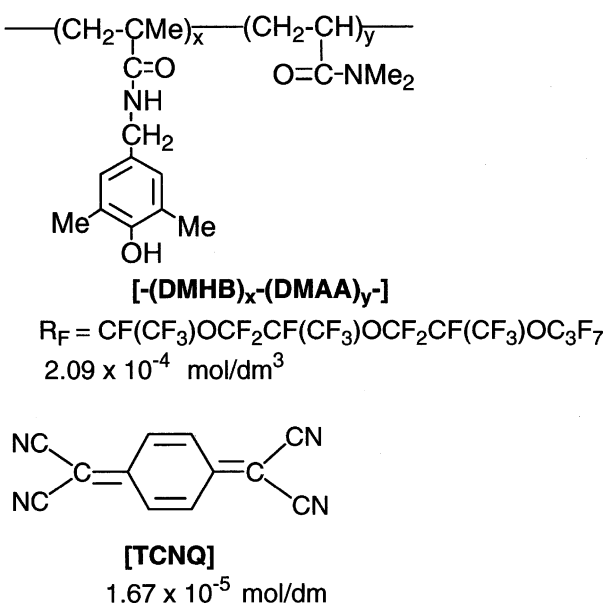


FIGURE 5 UV spectra of THF solutions of TCNQ in the presence of -$(DMHB)_x$-$(DMAA)_y$- co-oligomers.

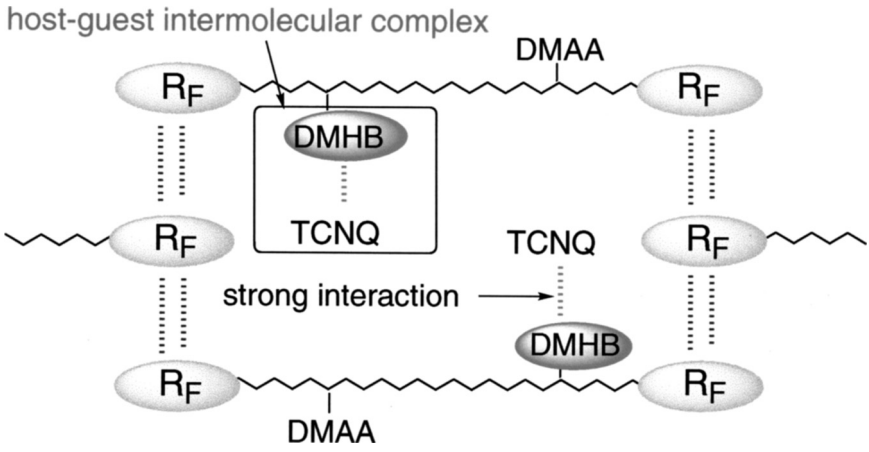


FIGURE 6 Schematic illustration for the interaction of self-assembled molecular aggregates formed by R_F-$(DMHB)_x$-$(DMAA)_y$-R_F and TCNQ: TCNQ could act as a guest molecule for the fluorinated host moieties.

weights were measured using a Varian Unity-plus 500 (500 MHz) spectrometer and a Shodex DS-4 pump and Shodex RI-71 Detector gel permeation chromatography (GPC) calibrated with standard polystyrene using tetrahydrofuran as the eluent, respectively. The surface tensions of 0.1 N NaOH solutions of the fluoroalkyl end-capped co-oligomers were measured at 30°C using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co.) with a glass plate. UV-visible spectra were obtained by using a Shimadzu UV-1600 spectrophotometer (Kyoto, Japan). XPS analyses were conducted by the use of Ar gas ion etching at the condition of 0.5 kV and 10 mA. Contact angles were measured by the use of a goniometer-type contact angle meter (ERMA G-1-1000) according to the authors' previously reported method [7].

Materials

N,*N*-Dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) were used as received from Kohjin Co., Ltd (Tokyo, Japan). Acrylic acid and BTRI were purchased from Wako Chemicals (Osaka, Japan) and Sigma-Aldrich Japan Inc. (Tokyo, Japan), respectively. DMHB was purchased from Monomer-Polymer & Dajac laboratories, Inc. (USA). TCNQ was purchase from Tokyo Kasei Kogyo Co., Ltd. (Tokyo,

Japan). A series of fluoroalkanoyl peroxides [$(R_FCOO)_2$] were prepared by a method described in the literature [8].

General Procedure for the Synthesis of Fluoroalkyl End-Capped Co-Oligomers

Perfluoro-2-methyl-3-oxahexanoyl peroxide (2.8 mmol) in 1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (100 g) was added to DMHB (2.6 mmol) and DMAA (28 mmol). The homogeneous solution was stirred at 45°C for 5 h under nitrogen. After evaporating the solvent, the crude product obtained was dialyzed [methanol/water:2/1 (vol.)] to give a α, ω–bis(perfluoro-1-methyl-2-oxapentylated) DMHB-DMAA co-oligomer (No. 1 in Table 1: 3.44 g). This co-oligomer exhibited the following spectra characteristics:

IR(ν/cm^{-1}) 3467 (OH), 1732[C(=O)], 1342(CF_3), 1244(CF_2); ^{1}H NMR($CDCl_3$) δ 0.65–3.21 (CH_3, CH_2, CH), 3.92–4.43 (CH_2), 6.72–7.12 (2H, aromatic protons); ^{19}F NMR($CDCl_3$, ext. CF_3CO_2H) δ – 4.57– – 7.79 (16F), – 54.23 (6F).

The other products obtained exhibited the following spectral characteristics:

R_F-$(DMHB)_x$-$(DMAA)_y$-R_F
$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 2 in Table 1)
IR(ν/cm^{-1}) 3442 (OH), 1730[C(=O)], 1342(CF_3), 1246(CF_2);
^{1}H NMR($CDCl_3$) δ 0.80–3.28 (CH_3, CH_2, CH), 3.40–3.92 (CH_2), 6.80–7.03 (2H, aromatic protons); ^{19}F NMR($CDCl_3$, ext. CF_3CO_2H)δ –4.03– –9.04 (26F), – 54.05– –54.23 (6F), – 69.58– –69.84 (2F).

R_F-$(DMHB)_x$-$(DMAA)_y$-R_F
$R_F = CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 3 in Table 1)
IR(ν/cm^{-1}) 3448 (OH), 1725[C(=O)], 1344(CF_3), 1248(CF_2);
^{1}H NMR($CDCl_3$) δ 0.68–3.62 (CH_3, CH_2, CH), 3.91–4.50 (CH_2), 6.71–7.02 (2H, aromatic protons); ^{19}F NMR($CDCl_3$, ext. CF_3CO_2H)δ –4.44– –8.91 (36F), –54.10– –54.88 (6F), –69.47– –69.99 (4F).

R_F-$(BTRI)_n$-R_F
$R_F = CF(CF_3)OC_3F_7$
IR(ν/cm^{-1}) 3432 (OH), 1728 [C(=O)], 1342(CF_3), 1242(CF_2);
^{1}H NMR($CDCl_3$) δ 0.59–3.40 (CH_2, CH_3, CH) 3.81–4.82 (CH_2), 6.81–8.29 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ –4.44– –7.14 (16F), – 53.46– –53.85 (6F).

R_F-(BTRI)$_x$-(ACA)$_y$-R_F
R_F=CF(CF_3)OC_3F_7 [No. 4 in Table 2]
IR(ν/cm^{-1}) 3452 (OH), 1711 [C(=O)], 1351(CF_3), 1242(CF_2);
^{1}H NMR($CDCl_3$) δ 0.42–2.58 (CH_2, CH_3, CH) 3.59–3.90 (CH_2), 6.30–7.59 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −5.53––7.92 (16F), −53.82––54.03 (6F).

R_F-(BTRI)$_x$-(ACA)$_y$-R_F
R_F = CF(CF_3)$OCF_2CF(CF_3)OC_3F_7$ [No. 5 in Table 2]
IR(ν/cm^{-1}) 3442 (OH), 1711 [C(=O)], 1351 (CF_3), 1242(CF_2);
^{1}H NMR($CDCl_3$) δ 0.40–3.80 (CH_2, CH_3, CH) 3.81–4.40 (CH_2), 6.40–8.23 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3,COOH) δ −5.45––9.04 (26F), −54.70––56.03 (6F); −71.11––71.29 (2F).

R_F-(BTRI)$_x$-(DMAA)$_y$-R_F
R_F = CF(CF_3)OC_3F_7 [No. 6 in Table 2]
IR(ν/cm^{-1}) 3442 (OH), 1720 [C(=O)], 1340(CF_3), 1242(CF_2);
^{1}H NMR($CDCl_3$) δ 0.63–2.22 (CH_2, CH_3), 2.25–3.69 (CH, CH_2, CH_3), 3.97–4.72 (CH_2), 6.98–8.50 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ − 5.64––7.43 (16F), −53.97––54.23 (6F).

R_F-(BTRI)$_x$-(DMAA)$_y$-R_F
R_F = CF(CF_3)$OCF_2CF(CF_3)OC_3F_7$ [No. 7 in Table 2]
IR(ν/cm^{-1}) 3456 (OH), 1712 [C(=O)], 1335(CF_3), 1244(CF_2);
^{1}H NMR($CDC1_3$) δ 0.71–2.01 (CH_2, CH_3), 2.31–3.80 (CH, CH_2, CH_3), 4.00–4.48 (CH_2), 6.99–8.37 (7H, aromatic protons); ^{19}F NMR ($CDC1_3$, ext. CF_3COOH) δ −4.31––7.82 (26F), − 54.08––54.42 (6F); −69.73––69.89 (2F).

R_F-(BTRI)$_x$-(ACMO)$_y$-R_F
R_F = CF(CF_3)OC_3F_7 [No. 8 in Table 2]
IR (ν/cm^{-1}) 3460 (OH), 1723 [C(=O)], 1358(CF_3), 1238(CF_2);
^{1}H NMR ($CDCl_3$) δ 0.75–2.18 (CH_2, CH_3), 2.25–4.65 (CH, CH_2), 7.00–8.37 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ − 5.56––7.35 (16F), − 53.90––53.97 (6F).

R_F-(BTRI)$_x$-(ACMO)$_y$-R_F
R_F=CF(CF_3)$OCF_2CF(CF_3)OC_3F_7$ [No. 9 in Table 2]
IR (ν/cm^{-1}) 3460 (OH), 1716 [C(=O)], 1352(CF_3), 1246(CF_2);
^{1}H NMR ($CDCl_3$) δ 0.65–5.80 (CH_2, CH_3, CH), 6.95–8.50 (7H, aromatic protons); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −4.29––7.63 (26F), − 54.00––54.31 (6F); − 69.55––69.76 (2F).

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